Phase equilibria in the $\text{YPO}_4\text{--Rb}_3\text{PO}_4$ system

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Abstract The phase equilibria occurring in the $\text{YPO}_4\text{--Rb}_3\text{PO}_4$ system were investigated by thermoanalytical methods, X-ray powder diffraction, and ICP-OES. On the basis of the obtained results, its phase diagram is proposed. It was found that the system includes two intermediate compounds $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ and $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$. The $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ compound melts congruently at 1300 °C. The $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ orthophosphate was previously unknown. This intermediate compound is high-temperature unstable and decomposes within the temperature range 1300–1330 °C to YPO_4 and $\text{Rb}_3\text{Y}(\text{PO}_4)_2$. The decomposition process is irreversible. It was found that the $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ orthophosphate is isostructural with $\text{Rb}_3\text{Yb}_2(\text{PO}_4)_3$ and crystallizes in the cubic system ($a = 1.70226$ nm).

Keywords Rubidium and yttrium orthophosphates · $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ · $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ · Phase diagram · Thermoanalytical investigations · X-ray powder diffraction

Introduction

Much study has been published about the binary orthophosphates $\text{M}_3^{\text{I}}\text{Ln}(\text{PO}_4)_2$ and $\text{M}_3^{\text{I}}\text{Ln}_2(\text{PO}_4)_3$ (where M^{I} = alkali metal or other monovalent metals, and Ln = a rare-earth element or Y or Sc) as well as those doped with lanthanide ions (see, e.g., [1–15]). Information in the literature are mainly focused on the preparation methods,

crystalline structure and application possibilities of those compounds. According to the data, these materials are of technological importance for applications in optics and electronics.

It results from experience, both of other workers' and ours, that the binary orthophosphates mentioned above may occur as intermediate compounds in the systems of the type $\text{LnPO}_4\text{--M}_3^{\text{I}}\text{PO}_4$ [6, 16–22]. Accordingly, in view of utilitarian character of those binary compounds, we undertook research on rubidium–yttrium orthophosphates, i.e., the $\text{YPO}_4\text{--Rb}_3\text{PO}_4$ system whose phase diagram was not published previously. We were also hoping to contribute to the knowledge about the chemical stability of the binary rubidium and yttrium phosphates.

From the literature information, it is known that $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ exists. According to [3], it melts at ~1255 °C. Its crystal structure is closely related to that of hexagonal glaserite (after [7]). Lattice parameters of $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ are: $a = 0.5695$, $c = 0.8122$ nm (after [3]); $a = 0.566754(3)$, $c = 0.807782(4)$ nm (after [7]). It was shown in [3] that heating the phosphates $\text{Rb}_3\text{Ln}(\text{PO}_4)_2$ (where Ln = Gd–Lu, Y, and Sc) above of 1250 °C results in their decomposition, which is accompanied by a mass loss due to an evaporation of rubidium orthophosphate; the decomposition process proceeds according to the scheme:

We have not succeeded in finding any literature data about the existence of an expected $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ binary rubidium and yttrium orthophosphate. However, the $\text{Na}_3\text{Y}_2(\text{PO}_4)_3$ binary sodium and yttrium orthophosphate is known [16]. This melts congruently at a temperature of 1635 °C, is stable down to room temperature and appears in two polymorphic modifications with the transition point 470 °C. Also, another orthophosphate, $\text{Rb}_3\text{Yb}_2(\text{PO}_4)_3$, is

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known [10], which crystallizes in the regular system (s.g. $I2_1/3$, $a = 1.6870(10)$ nm, $Z = 16$). It melts incongruently at 1450 K and decomposes in the temperature range from 1450 to 1541 K according to the reaction scheme:

The parent orthophosphates YPO_4 and Rb_3PO_4 are known to congruently melt at 2150 [24] and 1450 °C [25], respectively. YPO_4 crystallizes in the tetragonal system (s.g. $I4_1/amd$; $a = 0.68840(3)$, $c = 0.60202(3)$ nm) [23]. Rb_3PO_4 appears in two polymorphic modifications: the low temperature one crystallizes in the orthorhombic system (s.g. Pnma , $a = 1.17362(2)$, $b = 0.81046(1)$, $c = 0.615167(9)$ nm [26]), and the high-temperature one does in the regular system (s.g. $\text{Fm}3$, $a = 0.844$ nm [27]). The Rb_3PO_4 is strongly hygroscopic; DTA/TG–heating curves indicated a mass loss (water losing) in the temperature range 100–430 °C. A slow loss of mass was observed, too, starting from about 1150 °C, which did not affect the stoichiometry of the orthophosphate [25].

In this article, the results of investigation of the YPO_4 – Rb_3PO_4 system are described and its phase diagram is proposed.

Experimental

Investigations of the phase equilibria in the YPO_4 – Rb_3PO_4 system were conducted using the thermoanalytical methods, X-ray powder diffraction and inductively coupled plasma optical emission spectroscopy (ICP-OES). The following commercial materials (all analytically pure) were used: Y_2O_3 (99.92%), H_3PO_4 (85%), Rb_2CO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$. Orthophosphates YPO_4 and Rb_3PO_4 were self-prepared.

Yttrium orthophosphate YPO_4 was obtained from the following solution: 0.4 wt% Y_2O_3 , 15 wt% P_2O_5 (as H_3PO_4), 84.6 wt% distilled water—as we reported earlier [24]. Rubidium orthophosphate Rb_3PO_4 was produced from a stoichiometric mixture of dry Rb_2CO_3 (dried at 250 °C) and $(\text{NH}_4)_2\text{HPO}_4$ [25].

Samples for investigations of the YPO_4 – Rb_3PO_4 system were synthesized by a solid state reaction. The synthesis was preceded by the following mechanical processing. The weight amounts (in the assumed stoichiometric ratios) of the substrates were shaken in a weighing bottle, rubbed in an agate mortar in acetone, dried at 120 °C, placed in platinum crucibles or encapsulated in platinum ampoules, and then sintered. The synthesis conditions (i.e., temperature and time of sintering) were determined experimentally. The obtained sinters were crushed and finely ground.

The thermoanalytical investigations were carried out using a SETSYS^{TM} (SETARAM) differential thermal analyzer (calorimeter) with balance. The device enables one to perform simultaneous TGA–DTA or TGA–DSC measurements in the temperature range from 20 to 1350 °C. Samples of weight 15–20 mg were placed in platinum crucibles and heated at a rate of 10°Cmin^{-1} in an atmosphere of argon. DTA and TG analyses were also carried out in the air, up to 1400 °C, by using a derivatograph type 3427 (MOM, Hungary) with a heating rate of 5°C min^{-1} , in platinum crucibles, and samples from 0.3 to 0.6 g. High-purity Al_2O_3 was used as the standard material. Temperature was measured by means of a Pt/PtRh10 thermocouple which was calibrated against the melting points of NaCl, K_2SO_4 , and $\text{Ca}_2\text{P}_2\text{O}_7$ and the transition point of K_2SO_4 .

The high-temperature experiments (above 1400 °C) were performed in a horizontal resistance furnace with molybdenum winding, under argon. Test samples, each weighing ca. 2 g, were pelletized and placed in a Pt/PtRh30 boat. The temperature, at which a sample was diffusing and got blurred in the field of observation to finally disappear, was read by means of an optical pyrometer. For the samples that melt in a range of temperature, the melting points determined are approximate. The optical pyrometer was calibrated against the melting points of Na_3PO_4 and $\text{Ca}_3(\text{PO}_4)_2$. The quenching-in-ice technique was also employed to determine the phases; a high-temperature vertical tubular furnace (20–1750 °C; Nabertherm RHTV 120–300/18) was used.

The phase purity of the self-prepared parent phosphates and the phase composition of both the sinters (i.e., synthesized by the solid state reaction) and the melted samples for the investigated system, were controlled by X-ray powder diffraction at room temperature. A SIEMENS D 5000 diffractometer were used. The ICDD PDF-4+ database and the structures reported in the literature were searched to detect the phases present in the samples. The quantitative analysis was performed using the ICP-OES techniques (spectrometer Vista-MPX, VARIAN, Australia).

Results and discussion

The YPO_4 – Rb_3PO_4 system was examined in the whole composition range and in up to 1800 °C. At the initial stage, non-equimolar mixtures of the orthophosphates YPO_4 and Rb_3PO_4 (and also YPO_4 , Rb_2CO_3 , and $\text{NH}_4\text{H}_2\text{PO}_4$) were examined by different thermoanalytical methods. During X-ray diffraction analysis of reaction products, it was observed that some XRD patterns showed reflections indicating the appearance of certain new phases. During investigating the phase equilibria, both in binary

and multicomponent systems, it is of primary importance to have possible intermediate phases identified. At the next stage, the attention was paid to intermediate compounds in the $\text{YPO}_4\text{--Rb}_3\text{PO}_4$ system.

According to the literature data [3, 7], a molar ratio of $\text{YPO}_4\text{:Rb}_3\text{PO}_4 = 1\text{:}1$ (34.4 wt% YPO_4 , 65.6 wt% Rb_3PO_4) corresponds to the $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ binary rubidium and yttrium orthophosphate. The other expected, unknown compound $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ should have a molar ratio of $\text{YPO}_4\text{:Rb}_3\text{PO}_4 = 2\text{:}1$ (51.14 wt% YPO_4 and 48.86 wt% Rb_3PO_4).

In order to obtain the $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ orthophosphate the procedure was as follows. The parent substances: (1) YPO_4 , Rb_2CO_3 , and $\text{NH}_4\text{H}_2\text{PO}_4$ were mixed in the molar ratio 2:3:2, and—after mechanical processing (see “Experimental” section)—were sintered at 250 °C for 5 h, continued at 950 °C for 72 h (applying intermediate grindings to insure a total reaction); (2) YPO_4 and Rb_3PO_4 were mixed in the molar ratio 1:1 and, after mechanical processing, sintered at 950 °C for 4 h.

The synthesis conditions of (1) and (2) were found from experimental tests. The phase composition of the sinters obtained via the above solid state processes was checked by X-ray monitoring. The product of synthesis (1) as well as (2), in the form of white powder, was phase purity $\text{Rb}_3\text{Y}(\text{PO}_4)_2$. According to [3], this phosphate melts at 1255 °C. Based on the present investigation using DTA-heating in the range from room temperature to 1350 °C we have found that $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ melts congruently at 1304 °C. Simultaneously, a slow gradual loss of mass about 3.2 wt% was observed on the TG-heating curve from a temperature of ~1225 °C. The XRD pattern, however, of the sample slowly cooled down from ~1304 °C to room temperature showed only reflections typical of $\text{Rb}_3\text{Y}(\text{PO}_4)_2$.

Consequently, a quantitative determination of rubidium, yttrium and phosphorus content was made for the samples:

- $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ as synthesized in the solid state (a sinter),
- $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ as melted at 1304 °C and cooled down to room temperature.

Quantitative analysis was performed using the ICP-OES method. It appeared that the content of yttrium, rubidium, and phosphorus was the same in both samples under analysis.

According to [3], $\text{Rb}_3\text{Ln}(\text{PO}_4)_2$ are high-temperature unstable and upon a long heating above 1250 °C decompose to Rb_3PO_4 and LnPO_4 . In contrast, we have observed that the decomposition process has a rather complex character. It results from X-ray diffractometry that $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ remains its stoichiometry both upon melting (1304 °C) and upon a short (15 min) heating at 1330 and 1350 °C. In each case a mass loss was about 0.8 wt%, but XRD patterns exhibited only $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ reflections.

Consequently, the investigation was continued by heating at 1400 °C for 1 h, which gave a mass loss of about 3.1 wt%. Once more any decomposition products expected after [3] were not found in the XRD pattern.

The scheme of thermal dissociation $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ given in [3], i.e.,

is a simplified form. According to [25], at starting temperature 1150 °C, Rb_3PO_4 slowly decomposes into rubidium oxide (gas phase) and phosphorus oxide (gas phase). What is more, the results [28, 29] indicate that lanthanide orthophosphates undergo thermal dissociation in the air above 1200 °C. The decomposition proceeds according to the scheme:

(where $\text{Ln}_x\text{P}_y\text{O}_z$ represents four oxyphosphate groups). According to, [28] YPO_4 decomposes above 1300 °C in the solid state.

The above discussed results in more detail elucidate the effect of the mass loss appearance during heating the $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ at high temperatures. The decomposition product YPO_4 (or yttrium oxyphosphates) are not visible in the XRD pattern due to their insignificant amounts of ~1 wt% (for the total mass loss 3.1 wt%). We have confirmed in the above mentioned investigation that, in accord with the results of [3, 7], $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ occurs in the temperature range interest as one polymorphic modification of the hexagonal structure, and its parameters are $a = 0.566095$, $c = 0.807379$ nm.

To verify the question about the existence of the $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ an attempt to synthesize it was made from the following parent substances.

- 1 YPO_4 , Rb_3PO_4
- 2 YPO_4 , $\text{Rb}_3\text{Y}(\text{PO}_4)_2$
- 3 YPO_4 , Rb_2CO_3 , and $\text{NH}_4\text{H}_2\text{PO}_4$.

After mechanical processing (see “Experimental” section), the above mixtures were pressed into pellets and placed in platinum crucibles or encapsulated in platinum ampoules to be sintered at different temperatures for different periods of time. The phase composition of the output sinters was identified by X-ray powder analysis at room temperature.

It was found that via solid state reaction of sintering an equimolar mixture of YPO_4 and $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ in the closed ampoules at 1200 °C for 3 h, a new compound of phase purity appears. The formula $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ was assigned to it. Phase transformation of $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ from room

Fig. 1 T, DTA and TG curves of $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ (in air atmosphere)

temperature to 1350 °C were investigated using DTA-heating (in the air). The results are shown in Fig. 1. A slower pace is clearly seen from the temperature curve (T) in the range 1300–1330 °C. The DTA curve revealed a strong and broad thermal effect. In turn, TGA curve showed a small change in slope (a laminar lowering) above the temperature 1210 °C, which indicated a slow gradual mass loss. This loss amounted to 2.8 wt% in the temperature range 1210–1350 °C.

To explain the high-temperature behavior of the $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ orthophosphate X-ray powder diffraction was employed. XRD pattern the sample quenched from 1350 °C showed only reflections typical of the orthophosphates YPO_4 and $\text{Rb}_3\text{Y}(\text{PO}_4)_2$. These results gave evidence for that $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ was decomposed into these phosphates, which reveals its high-temperature instability. Accordingly, we found it necessary to examine the phase composition of $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ above the temperature 1200 °C. Eight samples of the $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ were prepared and placed into the furnace pre-heated to 1200 °C, and next each successively was heated to a higher and higher temperature of the series 1250, 1280, 1300, 1310, 1320, 1330, and 1340 °C. Each of seven samples had been heated at a given temperature for 10 min and then quenched. The eighth sample was cooled from 1340 °C to room temperature. The decomposition products appeared on the XRD pattern at 1330 °C. XRD pattern of 1340 °C showed only YPO_4 and $\text{Rb}_3\text{Y}(\text{PO}_4)_2$. These new phases alone remained on the XRD pattern of the sample (i.e., eighth) cooled down to room temperature.

On the basis of the above results of thermal and X-ray investigation it was assumed that the $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ decomposes in the temperature range approximately from 1300 to 1330 °C according to the reaction scheme:

the decomposition reaction is irreversible.

The X-ray study of $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ was performed using Siemens D5000 diffractometer (Brag-Brentano geometry, Ni filter, reflected pattern, CuK_α radiation). Pattern was taken with 2θ step of 0.02°, in the 5°–61° range and the counting time of 10 s at each point. Basing on the literature data [10], concerning the structure types of $\text{A}_3\text{B}_2(\text{X}^\text{V}\text{O}_4)_3$ compounds it was determined that the studied $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ compound is isostructural with $\text{Rb}_3\text{Yb}_2(\text{PO}_4)_3$ compound (s.g. $\text{I}2_13$ (199), $a = 1.687$ nm). In order to refine lattice parameters, the Rietveld Profile Refinement method was exploited using Rietica software [30]. As a result of refining, the lattice parameter $a = 1.70226$ nm (with derived Bragg R factor = 0.61) was calculated for the studied $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$. Peak positions and integrated intensities are given in Table 1.

Taking into account the conditions of $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ and $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ synthesis, their high-temperature instability like that of the Rb_3PO_4 , in order to obtain equilibrium samples the YPO_4 – Rb_3PO_4 system was studied by using three series of samples. These samples were:

- (1) non-equimolar mixtures of YPO_4 and $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ —to determine the phase equilibria within the composition range from 0 to 48.86 wt% Rb_3PO_4 ,
- (2) non-equimolar mixtures of $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ and $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ orthophosphates—to determine the phase equilibria within the composition range from 48.86 to 65.6 wt% Rb_3PO_4 ,
- (3) non-equimolar mixtures of $\text{NH}_4\text{H}_2\text{PO}_4$, dry Rb_2CO_3 and $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ —to determine the phase equilibria within the composition range from 65.6 to 100 wt% Rb_3PO_4 . The mixtures, after mixing and grinding in acetone, were dried at 120 °C and heated at 300 °C for 4 h, at 500 °C for 4 h, at 900 °C for 10 h, and at 1000 °C for 20 h (with intermediate grindings to insure a total reaction). The mixtures of the above items (1) and (2), after the mechanical processing, were synthesized via the solid state reaction by sintering at 1150 °C for 1 h. The sinters obtained were crushed and finely ground, to be finally investigated using thermoanalytical methods and X-ray powder diffraction.

Based on these results, the phase diagram of the YPO_4 – Rb_3PO_4 system was constructed (Fig. 2). The points marked with circles concern temperatures at which thermal effects appeared on the DTA-heating curves. Notation for

Table 1 Results of refinement procedure of XRD pattern of $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$

No.	2θ	$d/\text{\AA}$	I_{calc}	I_{obs}	Diff	ESD	h k l	
1.	18.037	4.9140	13.26	13.59	0.33	0.16	2 2 2	
2.	19.496	4.5494	10.83	10.92	0.08	0.11	1 2 3	m
3.	20.856	4.2557	50.86	51.16	0.31	0.42	0 0 4	
4.	22.137	4.0122	4.00	4.13	0.13	0.05	0 3 3	m
5.	23.351	3.8063	2.36	2.45	0.09	0.03	0 2 4	m
6.	24.508	3.6292	54.03	54.32	0.28	0.43	2 3 3	m
7.	26.68	3.3385	13.13	13.09	−0.04	0.09	0 1 5	m
8.	28.7	3.1079	80.65	80.28	−0.37	0.41	1 2 5	m
9.	29.663	3.0092	1000.00	999.76	−0.25	2.28	0 4 4	
10.	30.598	2.9193	0.42	0.43	0.01	0.01	0 3 5	m
11.	31.507	2.8371	1.08	1.13	0.05	0.01	0 0 6	m
12.	32.394	2.7614	22.09	22.07	−0.02	0.16	1 1 6	m
13.	33.26	2.6915	1.91	1.99	0.08	0.03	0 2 6	m
14.	34.106	2.6266	8.10	8.24	0.14	0.09	1 4 5	m
15.	34.934	2.5663	42.76	42.44	−0.32	0.34	2 2 6	
16.	35.745	2.5099	1.64	1.72	0.08	0.02	1 3 6	m
17.	36.541	2.4570	48.67	48.44	−0.23	0.39	4 4 4	
18.	37.322	2.4074	0.01	0.01	0.00	0.00	0 1 7	m
19.	38.089	2.3606	2.56	2.62	0.07	0.04	0 4 6	m
20.	38.844	2.3165	8.57	8.59	0.02	0.08	1 2 7	m
21.	39.586	2.2747	9.65	9.73	0.08	0.10	2 4 6	m
22.	40.317	2.2352	0.09	0.08	−0.01	0.00	0 3 7	m
23.	41.746	2.1619	2.32	2.38	0.07	0.03	1 5 6	m
24.	42.446	2.1279	131.13	130.30	−0.82	0.72	0 0 8	
25.	43.137	2.0954	10.87	10.87	0.00	0.09	1 1 8	m
26.	43.819	2.0643	5.12	5.15	0.03	0.06	0 2 8	m
27.	44.493	2.0346	26.55	26.47	−0.08	0.21	3 5 6	m
28.	45.159	2.0061	5.67	5.74	0.06	0.07	0 6 6	m
29.	45.817	1.9788	3.03	3.03	0.00	0.03	0 5 7	m
30.	46.467	1.9527	0.03	0.03	0.00	0.00	2 6 6	
31.	47.111	1.9274	6.00	6.02	0.02	0.07	2 5 7	m
32.	47.749	1.9032	49.01	48.92	−0.10	0.31	0 4 8	m
33.	48.379	1.8799	1.24	1.26	0.02	0.02	0 1 9	m
34.	49.004	1.8573	3.90	3.99	0.09	0.05	2 4 8	m
35.	49.623	1.8356	12.09	12.08	−0.01	0.09	1 2 9	m
36.	50.236	1.8146	9.61	9.81	0.19	0.13	4 6 6	
37.	50.844	1.7943	1.63	1.65	0.02	0.02	0 3 9	m
38.	52.044	1.7558	9.23	9.29	0.07	0.08	2 3 9	m
39.	52.637	1.7374	216.12	216.12	0.00	0.95	4 4 8	
40.	53.225	1.7196	2.95	2.96	0.00	0.03	0 7 7	m
41.	53.809	1.7023	2.21	2.24	0.03	0.03	0 0 10	m
42.	54.388	1.6855	2.49	2.52	0.04	0.04	1 1 10	m
43.	54.963	1.6692	4.47	4.49	0.02	0.05	0 2 10	m
44.	55.534	1.6534	1.55	1.58	0.02	0.02	0 5 9	m
45.	56.102	1.6380	9.96	10.06	0.10	0.12	2 2 10	m
46.	56.665	1.6231	5.89	5.91	0.02	0.05	1 3 10	m
47.	57.781	1.5943	3.52	3.55	0.04	0.04	1 7 8	m

Table 1 continued

No.	2θ	$d/\text{\AA}$	I_{calc}	I_{obs}	Diff	ESD	h k l	
48.	58.334	1.5805	4.09	4.11	0.02	0.04	0 4 10	m
49.	58.884	1.5671	13.83	13.85	0.03	0.12	1 6 9	m
50.	59.431	1.5539	7.12	7.16	0.04	0.09	2 4 10	m
51.	59.974	1.5412	0.45	0.45	0.00	0.01	0 1 11	m
52.	61.052	1.5165	4.95	4.97	0.02	0.05	1 2 11	m
53.	61.587	1.5046	55.90	55.98	0.09	0.44	0 8 8	

Fig. 2 Phase diagram of the system $\text{YPO}_4\text{--Rb}_3\text{PO}_4$; open circle, filled circle DTA-heating (filled circle temperatures of full $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ decomposition), x optical

the composition range from 0 to about 55 wt% Rb_3PO_4 is as follows: (i) open circles (above 1250 °C) show temperatures of $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ decomposition onset, (ii) filled circles show temperatures of full $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ decomposition. The thermal effects accompanying the initial and final stages of $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ decomposition gradually diminish to finally vanish. Liquidus curve could not be drawn in the above composition range because of the high-temperature instability of the intermediate compounds together with their complicated thermal dissociation. Also, we failed in an attempt to determine the melting points of the samples of composition range under discussion. Samples heated in the horizontal furnace (see “[Experimental](#)” section) vanished from the pyrometer field of view still before being fully melted, which appeared after cooling to room temperature. A lesser or larger partial melting of the

samples was connected with their composition. Temperature that was read by using the optical pyrometer just in the moment of vanishing from the visual field is marked by x in Fig. 2.

In the Rb_3PO_4 -rich part, of the composition range 48.86–100 wt% Rb_3PO_4 , two eutectics occur. The eutectic mixture e_1 melts at 1250 °C; its composition is 54 wt% $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ and 46 wt% $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$. The eutectic mixture e_2 melts at 1225 °C; its composition is 36 wt% Rb_3PO_4 and 64 wt% $\text{Rb}_3\text{Y}(\text{PO}_4)_2$. Polymorphic transformation $\alpha/\beta\text{-Rb}_3\text{PO}_4$ in the pure compound occurs at the temperature of 1040 °C. In the composition range $\text{Rb}_3\text{Y}(\text{PO}_4)_2\text{--Rb}_3\text{PO}_4$, the polymorphic transformation is recorded on DTA-heating curves as strong endothermal effects. Their onset is the temperatures range of 1010–1040 °C.

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